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(54) PRODUCTION OF ESTERS OF EPOXIDISED STEARIC ACID

(71) We, DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany, of 9 Weissfrauenstrasse, Frankfurt (Main), Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of esters of epoxidised stearic acid by epoxidising esters of unsaturated fatty acids with percarboxylic acids from mixtures, containing saturated and unsaturated fatty acids with up to 18 carbon atoms, or their esters and more particularly from natural oils and fats.

Esters of aliphatic and cycloaliphatic alcohols with epoxidised higher fatty acids have considerable significance as plasticisers, especially in the processing of polyvinyl chloride. These esters of epoxidised higher fatty acids, principally epoxy stearic acid, can be obtained by epoxidising the corresponding esters of the unsaturated fatty acids (Ind. Eng. Chem. 47 (1955), 147—148; Encyclopedia of Polymer Science, 1967, Vol. 6, 83—102). These esters of the unsaturated higher fatty acids are obtained in turn either by esterifying the free unsaturated acids or by transesterifying certain esters of these unsaturated acids with aliphatic or cycloaliphatic alcohols. Starting substances for the production of the unsaturated acids or their esters include principally natural oils and fats although they have to be initially split up into the unsaturated and saturated fractions. The oils and fats are split up by pressing, low-temperature crystallisation and filtration processes (D. Osteroth, *Natürliche Fettsäuren als Rohstoffe für die chemische Industrie*, Ferdinand Enke Verlag, Stuttgart, 1966, 50—51), or by a

hydrophilisation process (J. Amer. Oil Chemists' Soc. 45 (1968) 471—474).

This process is both complicated and expensive. 45

The present invention provides a process for the production of esters of epoxidised stearic acid from a mixture, containing saturated and unsaturated fatty acids with up to 18 carbon atoms or their esters, wherein those unsaturated and saturated fatty acids or their esters present in the mixture, which are not already esters with an alkanol with 1 to 3 carbon atoms, are converted into esters with an alkanol with 1 to 3 carbon atoms, the unsaturated fractions are epoxidised with a percarboxylic acid in the mixture and the mixture is subjected to distillation under reduced pressure to separate off the epoxy stearic acid ester which is optionally converted by transesterification into other esters. 55

By virtue of the process according to the invention, it is possible to obtain the required epoxy stearic acid esters from different kinds of mixtures of unsaturated and saturated higher fatty acids or their esters without any need for the starting mixtures to be split up before epoxidation into the unsaturated and saturated fractions by complicated methods. The only requirement which has to be satisfied is that the unsaturated and saturated fatty acids should be present in the form of esters of an alkanol with 1 to 3 carbon atoms for epoxidation. The action of the percarboxylic acids on an ester mixture of this kind leaves the saturated fractions unchanged, whilst the unsaturated fractions are converted into epoxy fatty acid esters. As a result, a mixture of esters with an alkanol with 1 to 3 carbon atoms of saturated fatty acids and epoxy fatty acids is formed. This mixture is separated by distillation under reduced pressure. The epoxy compounds undergo little or no decomposition during distillation so 85

[Price 25p]

that epoxy stearic acid esters can be obtained in very high yields and in a highly pure form. This is surprisingly because experience has shown that epoxy components of this kind

5 are thermolabile and are readily converted under the effect of heat into other compounds such as for example keto compounds and into polymers (Fette, Seifen, Anstrichmittel 67 (1965) 190—194).

10 If desired, the esters of epoxy stearic acid with an alkanol with 1 to 3 carbon atoms thus obtained can be converted into any other desired esters by transesterification in the presence of an alcoholate of an alkanol with 15 1 to 6 carbon atoms with an element from the second to fifth groups of the Periodic System as catalyst. Surprisingly, the epoxy structure is left unaffected by the transesterification reaction although splitting of the epoxide ring would be expected from previous experience in transesterification reactions.

20 Suitable starting materials include above all the usual oils and fats such as peanut oil, olive oil, palm oil, cotton seed oil, solza oil, sesame oil, soya bean oil, sunflower oil, linseed oil, perilla oil, oiticia oil, fish oil, train oil, tung oil, especially beef tallow, or optionally differently produced mixtures of higher fatty acids containing unsaturated fractions or their esters.

30 So far as the practical application of the process according to the invention is concerned, the mixtures of the fatty acids with up to 18 carbon atoms to be epoxidised must be in the form of esters of alcohols with 1 to 3 carbon atoms, i.e. in the form of propyl, ethyl or, in particular, methyl esters. Other compounds, non-esterified fatty acids or other esters such as the glycerol esters present in the oils and fats, are converted into the esters of alkanols with 1 to 3 carbon atoms.

40 C_1 to C_{10} percarboxylic acids are principally used for epoxidation, aliphatic C_1 to C_6 percarboxylic acids being particularly suitable. Peracetic acid is preferred. The percarboxylic acids are best used in solution in organic solvents. Although it is also possible to use aqueous percarboxylic acids, it is advisable in this case to add an organic solvent as solution promoter. Suitable solvents include inert liquids in which the substances to be reacted are adequately soluble, for example esters. Lower alkyl esters of acetic acid such as ethyl acetate are preferred. The reaction is generally carried out at a temperature of from 0 to 90°C and preferably at a temperature of from 25 to 70°C.

50 To recover the epoxy stearic acid esters from the reaction mixture, the solvent is initially removed from the reaction mixture at reduced pressure, after which the epoxy fatty acid esters are separated from the esters of the saturated fatty acids by fractional distillation under greatly reduced pressure. 65 Distillation can be carried out in distillation

apparatus such as for example a packed column which is provided with a heating jacket and, optionally, with additional heating in the sump.

Distillation is advantageously carried out 70 continuously. In this particular embodiment, it is advisable to introduce the mixture to be separated into the distillation column approximately in the middle thereof in the vapour phase in the form of a uniform stream. 75 To this end, it is evaporated under greatly reduced pressure in a preceding evaporator which also works in a continuous cycle, for example a falling-film evaporator. Any relatively high boiling fractions such as polymers 80 for example that are still present in the mixture can be simultaneously separated off in this preceding evaporator. Pressures and temperatures are governed by the type of compounds present in the mixture to be separated. In 85 general, pressure of from 0.1 to 10 Torr are applied. Accordingly, the boiling temperatures are substantially in a range from 100 to 250°C.

If desired, the epoxy stearic acid esters of 90 alkanols with 1 to 3 carbon atoms thus obtained may be converted into other esters. As mentioned above alcoholates are used as transesterification catalysts, suitable alcoholates being those of C_1 to C_4 alkanols, with elements from the Second to Fifth Group, especially from the Fourth Group of the Periodic System of Elements. It is preferred to use a titanium propylate or a titanium butylate 95 such as titanium tetraisopropylate or titanium tetrabutylate. 100

An alcohol component of relatively high boiling point is preferably introduced during the transesterification reaction and the transesterification temperature selected in such a way that the original alcohol component which boils at a relatively low temperature is continuously distilled off from the transesterification mixture. Transesterification proceeds particularly smoothly with aliphatic C_3 to C_{10} 110 alcohols even when the alcohols are branched or with cycloaliphatic alcohols with C_3 to C_6 rings which are optionally substituted by alkyl groups. Of these alcohols, isobutanol, 2-ethyl hexanol and cyclohexanol are mentioned in particular. The alcohols are used either in stoichiometric quantities or in over-stoichiometric quantities and preferably in an excess of from 10 to 100 ml %. The reaction catalysts are usually employed in concentrations of less than 5 mol % and preferably from 0.1 to 1.0 mol %, based on the mixture of ester to be transesterified and alcohol to be introduced. 120

Conventional techniques such as distillation, 125 extraction and filtration for example are used for recovering the epoxy stearic acid ester formed in pure form from the reaction mixture. The alcoholates are best removed by splitting them into the alcohols and metal 130

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oxides or metal hydroxides by treatment with water vapour.

The invention is illustrated by the following Examples.

5 Example 1

2700 g of fatty acid methyl ester prepared from beef tallow and showing the following characteristics were used:

10	Iodine number	44
	Ester number	197
	GC-analysis:	
	less than C_{16}	5.1%
	C_{16}	30.9%
	C_{18} saturated	22.3%
15	C_{18} unsaturated	34.0%
	remainder	7.6%

2700 ml of ethyl acetate were added to the fatty acid methyl ester, followed by the drop-

wise addition to this mixture with vigorous stirring of 630 g of aqueous 56.5% per- 20
acetic acid. The temperature of the mixture was prevented from rising beyond 25°C by cooling with ice. Stirring of the mixture was continued until, after a total of approxi- 25
mately 7 hours, the reaction was over. The two phases formed were separated. The aqueous phase was extracted with 500 mol of ethyl acetate, and the resulting extract added to the organic phase. The organic phase was washed repeatedly with water and then with 30
5% aqueous soda solution and then with water again, and finally was freed from the solvents under reduced pressure. The reaction mixture left, 2771 g, was crystal clear. 1600 g of this reaction mixture were subjected to fractional 35
distillation under reduced pressure in a vacuum jacketed packed column, the following results being obtained:

40	Fraction	Boiling point/pressure (°C _{Torr})	Quantity (g)	Epoxide content (%)*
	1	130 _{0.5}	304	1.5
	2	130 _{0.5} to 150 _{0.4}	520	7.2
	3	150 _{0.4} to 167 _{0.7}	93	39.0
	4	167 _{0.4} to 167 _{0.7}	11	78.9
45	5	169 _{0.7} to 205 _{0.4}	505	93.2
	residue		112	18.7

*Figures based on the methyl epoxy stearate content of the particular fraction.

Fractions 3 to 5 were redistilled. A total of 483 g of methyl epoxy stearate were recovered, corresponding to a yield of 86%, based on the quantity of oleic acid ester present in the starting mixture. The methyl epoxy stearate had an epoxide number of 5.05 and, accordingly, was 98.5% pure.

55 Example 2

The procedure was as described in Example 1, except that epoxidation was carried out at 55°C for a reaction time of 4 hours. After fractional distillation and redistillation, 466 g of methyl epoxy stearate were obtained, corresponding to a yield of 83% based on the quantity of oleic acid ester present in the starting mixture. The methyl epoxy stearate had an epoxide number of 4.99 and, accordingly, was 97.5% pure.

Example 3

The procedure was as described in Example 1, except that epoxidation was carried out with 1296 g of 27.4% peracetic acid dissolved in ethyl acetate. After fractional distillation and dedistribution, 504 g methyl epoxy stearate were obtained, corresponding to a yield of 90%, based on the quantity of oleic acid ester present in the starting mixture. The methyl epoxy stearate had an epoxide number of 5.07 and, accordingly, was 99.0% pure.

Example 4

A mixture of fatty acid methyl esters similar to that described in Example 1, prepared from beef tallow, was treated with peracetic acid by the procedure described in Example 1. 3510 g of the washed reaction mixture substantially free from solvents was distilled under reduced pressure in order to separate off the epoxy stearic acid methyl ester. A packed column with an electrically heated jacket and with additional heating in the sump of the column which was preceded by a falling-film evaporator was used for this purpose. The reaction mixture to be split up was delivered in the form of a uniform stream, evaporated in the falling-film evaporator and fed from the falling-film evaporator into the distillation column at the middle thereof in the form of a vapour. Relatively high boiling fractions, amounting to around 2%, were separated off in the falling-film evaporator in which the pressure amounted to around 2.5 Torr and the temperature to between 180 and 190°C. The methyl esters of the saturated fatty acids distilled over at the head of the distillation column at 155 to 158°C/1.0 to 1.1 Torr, whilst the methyl ester of epoxy stearic acid was run off from the sump of the column at 200 to 205°C/3.5 to 4 torr. The yield of epoxy stearic acid methyl ester came to 1190 g, corresponding to 96%, based on the oleic acid methyl ester which was

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used in the mixture of fatty acid methyl esters obtained from the beef tallow. The epoxy stearic acid methyl ester had an epoxide number of 5.20 as against a theoretical of 5.12, and was found by gas chromatography to be 98.5% pure.

Example 5

372 g (120 mol) of the methyl epoxy stearate obtained in accordance with Example 1 were mixed with 310 g (2.39 mol) of 2-ethyl hexanol and 0.8 g of titanium tetraisopropylate, and the resulting mixture heated to around 130°C in a distillation retort surmounted by a column. Methanol which was liberated during the reaction distilled over and was collected as distillate. The reaction mixture was heated until the distillation of methanol stopped. The mixture was then subjected to distillation with steam during which the excess 2-ethyl hexanol distilled over in the form of an azeotropic mixture boiling at 99°C with 80% of water. At the same time, the titanium tetraisopropylate was split up. Following removal of the 2-ethyl hexanol and cooling of the residual mixture, the aqueous phase formed was separated following the addition of 200 ml of light petrol. This aqueous phase was extracted with 100 ml of light petrol. The extract was added to the organic phase. The organic phase was then filtered clear with the assistance of 10 g of a filter aid, dried with Na₂SO₄ and freed from solvent under reduced pressure. 430 g (87%) of 2-ethyl hexyl-1 epoxy stearate were obtained, showing the following characteristics:

Epoxide number	3.47 (theoretical 3.89)
Ester number	139
Acid number	0.5
n_D^{20}	1.4520
Gardner colour index	2
Hazen colour index (DIN 53 503)	110

Example 6

218 g (0.75 mol) of the methyl epoxy stearate were reacted as in Example 5 with 150 g (1.5 mol) of cyclohexanol in the presence of 0.2 g of titanium tetrabutylate. On completion of the reaction, most of the excess cyclohexanol was initially recovered by distillation under reduced pressure, after which the further procedure was as described in Example 5. 245 g (86%) of cyclohexyl epoxy stearate with an epoxide number of 3.96 as against a theoretical of 4.21 were obtained.

Example 7

The procedure was as described in Example 5 except that 218 g (0.75 mol) of the methyl epoxy stearate were reacted with 111 g (1.5 mol) of isobutanol in the presence of 0.4 g of titanium tetraisopropylate. 218 g (82%) of isobutyl epoxy stearate with an epoxide number of 4.47 as against a theoretical of 4.52 were obtained.

WHAT WE CLAIM IS:—

1. A process for the production of esters of epoxidised stearic acid from a mixture, containing saturated and unsaturated fatty acids with up to 18 carbon atoms or their esters, wherein those unsaturated and saturated fatty acids or their esters present in the mixture which are not already esters with an alkanol with 1 to 3 carbon atoms, are converted into esters with an alkanol with 1 to 3 carbon atoms, the unsaturated fractions are epoxidised with a percarboxylic acid in the mixture and the mixture is subjected to distillation under reduced pressure to separate off the epoxy stearic acid ester.
2. A process as claimed in Claim 1, wherein the alkanol with 1 to 3 carbon atoms is methanol.
3. A process as claimed in Claims 1 or 2, wherein the percarboxylic acid contains from 1 to 10 carbon atoms.
4. A process as claimed in claim 3, wherein the percarboxylic acid is aliphatic and contains from 1 to 5 carbon atoms.
5. A process as claimed in Claim 4, wherein the percarboxylic acid is peracetic acid.
6. A process as claimed in any of claims 1 to 5, wherein the epoxidation reaction is carried out in water, ethyl acetate or a mixture thereof as a solvent.
7. A process as claimed in any of claims 1 to 6, wherein distillation is carried out at a pressure of from 0.1 to 10 Torr.
8. A process as claimed in claim 7, wherein distillation is carried out continuously.
9. A process as claimed in any of claims 1 to 8, wherein the resulting ester is converted into another ester by transesterification using an alcoholate of an alkanol with 1 to 6 carbon atoms with an element from the Second to Fifth groups of the Periodic System is used as a transesterification catalyst.
10. A process as claimed in Claim 9, wherein the catalyst is a titanium propylate or a titanium butylate.

11. A process for the production of an epoxidised stearic acid ester substantially as hereinbefore described with reference to any of the Examples.

- 5 12. An epoxidised stearic acid ester when produced by a process as claimed in any of claims 1 to 11.

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